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## DRAWINGS ATTACHED

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(54) DEPOSITING EPITAXIAL LAYER OF SILICON FROM  
 A MIXTURE OF AN INERT GAS

(71) We, RCA CORPORATION, a corporation organised under the laws of the State of Delaware, United States of America, of 30 Rockefeller Plaza, City and State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improved methods of fabricating crystalline semiconductive layers, and more particularly to improved methods of depositing epitaxial layers of crystalline silicon on substrates.

Epitaxial layers of semiconductors such as silicon have been deposited on substrates by forming a halogen compound of the semiconductor; passing vapors of the compound over the substrate; and admixing hydrogen into the vapors to reduce the halogen compound and deposit a layer of the semiconductor on the substrate. Epitaxial silicon layers have also been deposited on a substrate by heating the substrate in an ambient consisting of a mixture of silane and hydrogen. For details of prior art methods of depositing epitaxial layers of semiconductive materials, see for example RCA REVIEW, December 1963, pp. 473—595. While satisfactory epitaxial layers have been deposited by these methods, improvement is desirable in such respects as increasing the speed of the deposition process, and improving the crystal quality or lattice perfection of the deposited silicon.

According to the invention there is provided a method of depositing an epitaxial silicon layer on at least one comprising positioning each said substrate on a heating element in a reaction chamber, the substrate surface to be deposited being uppermost and flowing a mixture of silane and an inert gas through said chamber while heating said substrate by means of said heating element, and shielding the upstream surface of said heating element and the upstream surface of said substrate from contact with said flowing mixture so that pre-

heating of said mixture prior to contact of said mixture with said substrate surface to be deposited is minimized. The mixture may include a gaseous substance which is a conductivity modifier in silicon. Turbulence in the flow of the mixture is minimized.

In the accompanying drawing:

The single figure is a cross-sectional view of apparatus useful in the practice of the invention.

Referring now to the drawing, suitable apparatus 10 for the practice of the invention comprises a refractory furnace tube 11. The furnace tube 11, which may for example consist of fused quartz, includes a reaction chamber 12 having at one end an inlet 13. The cross-sectional area of the inlet 13 is less than that of the reaction chamber 12, but the upper surfaces of the inlet 13 and the reaction chamber 12 are coplanar and continuous. The apparatus 10 is provided with a gas entry 14 at one end of the inlet 13. A gas outlet 15 is provided at one end of the reaction chamber 12. The apparatus 10 includes a water jacket 16 which surrounds the adjoining portions of the reaction chamber 12 and the inlet 13. An RF heating coil 17 is provided around that portion only of the water jacket 16 which is adjacent the reaction chamber 12.

Inside the reaction chamber 12, a susceptor 18 which serves as the heating element is positioned at that end of the chamber 12 to which the inlet 13 is joined. Since the cross-sectional area of the inlet 13 is less than that of the chamber 12, while the upper surfaces of the chamber 12 and the inlet 13 are continuous, there is a vertical wall 19 in the reaction chamber 12 where the chamber 12 joins the inlet 13. The susceptor 18, which suitably consists of a graphite block coated with a layer of silicon carbide, is positioned immediately adjacent wall 19 so that the upper surface of the susceptor 18 is substantially parallel to and coplanar with the lower surface of the inlet 13. The substrate or substrates 20 on which the silicon layer is to be deposited are positioned on the upper surface

of the susceptor 18. In practice, it is more economical to deposit a silicon layer on a plurality of substrates 20 during each run. Since the substrates 20 utilized are generally less than 1 mm thick, the substrate surface on which deposition takes place is substantially coplanar with the lower surface of inlet 13.

A mixture of silane and an inert gas may be passed through the apparatus 10 in the direction shown by the arrows from the gas entry 14 to the gas outlet 15. As the gas stream enters the reaction chamber 12 via the inlet 13, it is cooled by the water jacket 16 until the moment that the stream enters the reaction chamber 12. Moreover, the gas stream entering the reaction chamber 12 has been passing through an inlet 13 of constant cross-section as the gas stream passes over the heated substrates 20. Furthermore, the substrate surface on which deposition takes place is close to and substantially coplanar with the lower surface of the inlet 13. As a result, turbulence in the gas stream passing over the substrates 20 is minimized. While the heating element 18 in this apparatus is an RF susceptor, it will be understood that other heating elements, such as an electrical resistance heater, may be utilized.

#### EXAMPLE I

A variety of substrates may be utilized in the practice of the invention, and the precise size, shape and composition of the substrates utilized is not critical. However, monocrystalline substrates are preferred when it is desired that the deposited silicon layer should be monocrystalline. In this example, the substrates utilized consist of synthetic monocrystalline alumina. Clear water-white varieties of this material are commercially available, and are known as sapphire. The sapphire substrates are suitably in the form of discs about 0.25 mm thick and 19 mm in diameter. Advantageously, the sapphire discs have been cut so that the major faces of the discs are at a 60° angle to the C axis of the sapphire crystalline lattice. Each sapphire substrate is polished smooth on one major face, and then degreased. Suitably, the sapphire disc is cleaned with ultrasonic energy in an organic solvent such as chloroform.

Referring now to the drawing, one or more substrates 20 are positioned on a heating element, such as the susceptor 18, in the reaction chamber 12 close to the vertical wall 19. In this example, a plurality of sapphire discs 20 are positioned on the susceptor 18 with the polished surface of each sapphire disc uppermost, and coplanar with the lower surface of the inlet 13, as described above. The apparatus 10 may be purged by a stream of palladium-diffused hydrogen. The substrates 20 are now preheated in an inert gas such as helium, neon, argon or nitrogen, to bring

them up to temperature. In this example, the sapphire substrates 20 are preheated in a stream of helium at a temperature of about 950°C.

Next, a mixture of silane and helium is passed through the apparatus 10 in the direction shown by the arrows with minimum turbulence in the gas flow. The amount of silane in the mixture is kept below 3 volume percent, and is preferably about 0.1 to 0.2 volume percent. The flow rate of the mixture may be varied to vary the deposition rate of the silicon layer on the substrates. In this example, the flow rate of the silane-helium mixture is 10 liters per minute. Under these conditions, the deposition rate of the silicon layer epitaxially deposited on the substrates is about 0.1 to 0.2 microns per minute. Deposition is continued for about 10 to 20 minutes, so that the total thickness of the epitaxial silicon layer deposited on each substrate is about 1 to 2 microns.

The silicon layer thus deposited on a sapphire substrate has been found to be monocrystalline, and of good quality. Moreover, little autodoping of the substrate by the aluminum atoms present in the sapphire substrates can occur because of the relatively low temperature of the deposition. The epitaxial monocrystalline layers thus deposited can be utilized to fabricate arrays of insulated-gate field-effect transistors, and other types of PN junction devices. For details, see for example P. H. Robinson and C. W. Mueller, TRANSACTIONS OF THE METALLURGICAL SOCIETY OF AIME, 236, pp. 265-274, March 1966.

A feature of this method of depositing layers on a substrate is that the heating element itself, and that surface of the substrate which faces upstream to the gas flow, is shielded from the gas flow by the wall 19. Hence, the premature heating of the molecules of the flowing gas, which occurs in prior art methods by contact of the gas with the heating element or with the upstream facing of the surface prior to contact of these gas molecules with the substrate surface on which deposition of the silicon layers is desired, is prevented, or is at least minimized. Such premature heating of the gas flow is undesirable because some of the silane molecules in the gas decompose, forming hydrogen and elemental silicon. The silicon thus formed cannot be a gas or vapor at these low temperatures, and hence becomes a cloud of solid particles. Some of these silicon particles deposit on the walls of the apparatus, where they are not desired. Those silicon particles which do deposit like dust on the desired surface of the substrate become part of the epitaxial layer, but the perfection of the epitaxial crystal lattice is thereby adversely affected, since the epitaxial layer becomes, as it were, an aggregate of particles, instead of

the desired highly regular lattice. In contrast, in the method of this invention, the silane in the gas flow is decomposed predominantly in contact with the desired surface of the substrate, and hence the epitaxial silicon layer on the desired surface of the substrate is deposited molecule by molecule to form a crystal lattice of high quality. The avoidance of premature heating of the gas stream prior to the deposition of the silicon layer helps to avoid premature decomposition of the silane and the formation of silicon dust.

#### EXAMPLE II

In the previous example, a pure mixture of silane and an inert gas was utilized for the deposition of an epitaxial silicon layer on a sapphire substrate. The silicon layers deposited in this manner are generally of high resistivity, and are usually of P type conductivity. Alternatively, low resistivity silicon layers of either P type or N type conductivity may be deposited on a crystalline substrate by the addition to the silane mixture of a gaseous substance which is capable of acting as a conductivity modifier in silicon. The gaseous conductivity modifier may consist of arsine or phosphine when N type silicon layers are desired, and may for example consist of diborane when P type silicon layers are desired. The amount of the gaseous conductivity modifier utilized is quite small, and is suitably about 50 to 100 parts per million of the silane and inert gas mixture.

In this example, sapphire substrates 20 are prepared and positioned on a heating element such as the susceptor 18, as described in Example I above. The apparatus 10 is purged by a flow of pure hydrogen. Next, the sapphire substrates 20 are heated in a flow of pure helium to a temperature of about 950°C. Then the flow of gas through the apparatus is changed to a mixture consisting principally of helium, but containing 0.1 volume percent silane and 100 parts per million of arsine. Under these conditions, an N type epitaxial layer of monocrystalline silicon is deposited on each sapphire substrate. The mobility of majority charge carriers in an N type silicon layer deposited as described has been found to be about 500 to 600 cm<sup>2</sup> per volt sec.

By substituting diborane for the arsine, P type silicon layers can be similarly deposited on a substrate. The resistivity of the deposited silicon layers can be varied over a range of 3 orders of magnitude, for example from about .008 ohm-cm to about 20 ohm-cm, by varying the concentration of the gaseous conductivity modifier in the silane mixture.

#### EXAMPLE III

In the two previous examples, the substrate consisted of sapphire, and the inert gas utilized was helium. In the present example, the

substrate consists of crystalline spinel, and the inert gas is argon.

The spinel utilized may consist of monocrystalline stoichiometric magnesium aluminate. Commercial crystalline spinels which are non-stoichiometric due to an excess of alumina may also be utilized. The spinel substrates are prepared, polished, and degreased as described in Example I above, and are then similarly positioned on the susceptor 18 with the polished surface of each substrate 20 uppermost. The spinel substrates are then heated in an ambient of flowing argon at a temperature of about 900°C. A gaseous mixture of argon and about 0.2 volume percent silane is then passed through the apparatus 10 in the direction indicated by the arrows, and passes over the spinel substrates 20 in such a manner that preheating of the silane and turbulence in the gas flow is minimized. Utilizing a flow rate for the argon-silane mixture of about 10 liters per minute, the deposition rate of the silicon layer on the spinel substrates is about 0.1 to 0.2 microns per minute. After an epitaxial silicon layer of the desired thickness has thus been deposited on the substrates, usually from 1 to 2 microns thick, the substrates are cooled to room temperature in an inert ambient. The silicon layer thus deposited on the spinel may be fabricated into semiconductor devices in the same manner mentioned above as the silicon layers deposited on sapphire.

In the same manner previously described in connection with sapphire substrates, the epitaxial crystalline silicon layers deposited on spinel substrates may be made N type by the addition of about 50 to 100 parts per million of arsine or phosphine to the argon-silane mixture. Alternatively, the silicon layers may be made P type by the addition of about 50 to 100 parts per million of diborane to the argon-silane mixture.

#### EXAMPLE IV

In the previous examples, the substrate utilized was an insulator. In the present example, the substrate utilized is monocrystalline silicon. The precise size, shape and conductivity of the silicon substrate is not critical. Suitably, the silicon substrate may be a thin slice of a monocrystalline ingot. In this example, the silicon substrate is a disc about 30 mm in diameter, about 0.1 mm thick, of N type conductivity, and low resistivity. The silicon disc is preferably cut so that the major faces of the disc are substantially parallel to the [111] crystal plane of the silicon lattice. Preferably, the major faces of each silicon disc or slice are lapped and polished, so that they are smooth and flat.

One or more such silicon substrates 20 are then positioned on the heating element, which may be a susceptor block 18 as described in Example I above. The substrates are then

heated in a flow of pure palladium-diffused hydrogen at a temperature of about 1200°C for about 15 minutes. Any film of silicon oxide or other impurity on the surface of the substrates 20 is thus removed.

The temperature is then dropped to 800°C by reducing the supply of electrical power to the RF heater 16. A mixture consisting of an inert gas, about 0.01 to 0.2 volume percent silane, and about 50 parts per million phosphine, is passed through the apparatus 10 in the direction shown by the arrows. The mixture flows over the silicon substrates 20 in the manner described above, so that turbulence in the flow is minimized. With a flow rate of about 20 liters per minute, and a mixture containing about 0.2 volume percent silane, a growth rate as high as 0.5 microns per minute was obtained at a temperature as low as 800°C. An N type epitaxial layer of monocrystalline silicon is thus deposited on each silicon substrate. Suitably, the silicon layer is about 5 microns thick. The subsequent utilization of such epitaxial silicon layers for the fabrication of semiconductor devices is well known to the art. See for example Mayer et al U.S. Patent 3,177,100, issued April 6, 1965.

In prior art methods, epitaxial silicon layers are deposited on silicon substrates at temperatures of at least 1000°C. Since the diffusion of conductivity modifiers into silicon practically ceases at temperatures below 1000°C, it follows that when epitaxial silicon layers are deposited on silicon wafers at temperatures as low as 800°C, then autodoping of the epitaxial layer by the substrate is minimized. Moreover, any PN junctions or impurity concentration profiles present in the silicon substrate will not be altered or disturbed by process steps conducted at temperatures as low as 800°C. For example, a first epitaxial layer of N type monocrystalline silicon can be deposited on a silicon substrate as described above. Then the mixture flowing through the apparatus can be changed to a mixture consisting of an inert gas, about 0.2 volume percent silane, and about 50 to 100 parts per

million diborane. A second and P type epitaxial silicon layer will thus be deposited on the first and N type epitaxial layer. However, because the temperatures utilized are as low as 800°C, the PN junction between the two epitaxial layers will be unusually abrupt. Such abrupt junctions are desirable for certain types of semiconductor devices.

#### WHAT WE CLAIM IS:—

1. The method of depositing an epitaxial silicon layer on at least one substrate comprising positioning each said substrate on a heating element in a reaction chamber, the substrate surface to be deposited being uppermost and flowing a mixture of silane and an inert gas through said chamber while heating said substrate by means of said heating element, and shielding the upstream surface of said heating element and the upstream surface of said substrate from contact with said flowing mixture so that preheating of said mixture prior to contact of said mixture with said substrate surface to be deposited is minimized.
2. The method as claimed in claim 1, wherein said mixture of silane and an inert gas contains a gaseous substance capable of acting as a conductivity modifier in silicon.
3. The method as claimed in claim 1, wherein said mixture passes into said reaction chamber through an inlet of uniform cross-section, said inlet cross-section being less than the cross-section of said reaction chamber, said substrate surface to be deposited being substantially coplanar with the lower surface of said inlet, so that said mixture passes over said substrate surface to be deposited with a minimum of turbulence in the flow.
4. The method of depositing an epitaxial silicon layer on a substrate substantially as described with reference to the single figure of the drawing.

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